Chapter Two The States of Substances

§2–1 Gases

一、 Ideal Gases

1 The Equation of State for Ideal Gases

Gases are involved in many chemical reactions. For example, oxygen, a gas, is one of the most important of all chemical reagents. Experimentally, it is not convenient to measure quantities of gas in the same manner that quantities of solids and liquids are measured, because any quantity of gas will occupy the entire volume of its container, regardless of the size of the container. Moreover, gases cannot be quantitatively transferred from one open vessel to another. However, in a container of a given size at a given temperature, the pressure exerted by a gas will depend on the quantity of that gas which is present. It will now be shown how the number of moles of a gas can be determined by measuring its volume, pressure, and temperature.

1) Boyle's Law

For a fixed mass of gas at constant temperature, the volume of the gas is inversely proportional to its pressure. This statement is known as Boyle's law. This law is approximately true for all gases, but it does not apply to liquids or solids. It is more exact if the pressure of gas is low and the temperature is relatively high. In mathematical form, the law may be represented as

$\underline{PV = k \quad (\text{constant} \quad T)}$

Since k is a constant, as P gets larger, V must get correspondingly smaller; thus V varies inversely with P.

2) **Charles' Law**

It may be determined experimentally that the volume of a given mass of gas at constant pressure varies approximately linearly with the temperature.

$T = t + 273^{o}$

The Kelvin temperature scale is based on concept of absolute zero; the zero temperature (-273^{o}) of the scale is the lowest temperature theoretically possible. The symbol for "degrees Kelvin" is K.

The volume of a given mass at constant pressure is directly proportional to its *absolute* temperature (T). This is a statement of **Charles' law**, which can be expressed mathematically as

$V = k'T$ (constant pressure)

3) The Equation of State for Ideal Gases

$\boldsymbol{PV = n\,RT}$

P: Pressure V: Volume T: absolute Temperature

n: the Number of Moles of Gas R: Constant

where n is the number of moles of gas in the sample and R is a constant which is characteristic of all gases. The numerical value of R depends, of course, on the units chosen to express *P*, *V*, and *T*.

It is found experimentally that at 0℃ and 1.00 atm pressure (STP), 1.00 mole of any gas occupies approximately 22.4 liters. Hence the gas constant R can be evaluated as follows:

$$R = \frac{PV}{nT} = \frac{(1.00\text{atm})(22.4\text{liters})}{(1\text{mole})(273\text{K})} = 0.0821 \text{ liter . atm /mole . K}$$

$$* \text{ SI:} \quad R = \frac{(101325\text{Pa})(22.4\times10^{-3}\text{m}^3)}{(1\text{mole})(273\text{K})} = \underline{8.314 \text{ Pa .m}^3\text{. mol}^{-1}\text{ . K}^{-1}}$$

$$= \underline{8.314 \text{ kPa .l . mol}^{-1}\text{ . K}^{-1}}$$

$$* = \underline{8.314 \text{ J. mol}^{-1}\text{ . K}^{-1}}$$

With the equation *PV* = *nRT*, it is possible to calculate the number of moles of a gaseous sample from pressure, volume, and temperature data. If the volume occupied by a certain mass of a pure gaseous substance is known at some temperature and pressure, it is possible to calculate the mass per mole of gas—the molecular weight.

Real gases do not follow Boyle's law or Charles' law exactly. Relatively great deviations are observed when a real gas is under high pressure and / or is at relatively low temperature. An ideal gas is defined as a gas which follows the gas laws exactly for all conditions of temperature and pressure. The equation *PV* = *nRT* is therefore referred to as the equation of state for an ideal gas. Real gases approach ideal behavior in the limit of very low pressure and relatively high temperature.

Another Equations: $PV = nRT = \frac{m}{M}RT$

$$PM = \frac{m}{V}RT = \rho RT$$

$$\frac{\rho}{P} = \frac{M}{RT}$$

2 The Law of Partial Pressures

Assuming that no chemical reaction occurs, when two or more different gases are put into the same container, the total pressure is merely the sum of the individual pressures of the different gases. In other words, each gas exerts a pressure independent of the others—as thought it were the only gas in the container. Hence the total pressure P is given by the sum of partial pressures,P_1 , P_2, etc.:

$$\boldsymbol{P} = P_1 + P_2 + \ldots$$

This relationship is known as **Dalton's law** of partial pressures.

$P_1 = n_1RT／V$, $P_2 = n_2RT／V$, $P_3 = n_3RT／V$,

$P_i = n_iRT／V$

$$n_{总} = n_1 + n_2 + n_3 + \ldots + n_i$$

(1) $P_{总} = P_1 + P_2 + P_3 + \ldots + P_i = \sum P_i$

(2) $P_1 ／ P_{总} = n_1RT／n_{总}RT = n_1／ n_{总}$

$P_i ／ P_{总} = n_iRT／n_{总}RT = n_1／ n_{总}$

$x_1 = n_1／ n_{总}$, $x_i = n_1／ n_{总}$,

$P_i = P_{总}\cdot n_i／n_{总} = P_{总}\cdot x_1$, $x_1 + x_2 + x_3 +\ldots +x_i = 1$

The application of Dalton's law is illustrated by the following examples.

Example

If 2.0 grams of N_2, 0.4 grams of H_2, and 9.0 grams of O_2 are put into a 1.00 liter container at 27℃, what is the total pressure in the container ?

The number of moles and the partial pressure of each gas is found:

T = 273 + 30 = 300 K

$n_{N2} = 2.0\text{g} / 28.0\text{g.mol}^{-1} = 0.071 \text{ mol}$

$P_{N2} = n_{N2} RT / V$

$$P_{N2} = \frac{(0.071\text{mol})(8.314\text{ kPa.l.mol}^{-1}\text{K}^{-1})(300\text{ K})}{1.00\text{ liter}} = 177\text{ kPa}$$

$n_{H2} = 0.4\text{g} / 2.0\text{g.mol}^{-1} = 0.20 \text{ mol}$

$P_{H2} = n_{H2} RT / V$

$$P_{H2} = \frac{(0.20\text{mol})(8.314\text{ kPa.l.mol}^{-1}\text{K}^{-1})(300\text{ K})}{1.00\text{ liter}} = 499\text{ kPa}$$

$n_{O2} = 9.0\text{g} / 32.0\text{g.mol}^{-1} = 0.28 \text{ mol}$

$P_{O2} = n_{O2} RT / V$

$$P_{O2} = \frac{(0.28\text{mol})(8.314\text{ kPa.l.mol}^{-1}\text{K}^{-1})(300\text{ K})}{1.00\text{ liter}} = 698\text{ kPa}$$

The total pressure is

$P = P_{N2} + P_{H2} + P_{O2} = 1374 \text{ kPa}$

The same result could have been attained by adding the number of moles of the individual gases and calculating the total pressure from

$P_{total} = n_{total} RT / V$

3 The Law of Diffusion for Gases

In the same T, P: $$\frac{\mu_A}{\mu_B} = \sqrt{\frac{\rho_B}{\rho_A}} = \sqrt{\frac{M_B}{M_A}}$$

μ: Diffusive Velocity ρ: Density

Applications: 1) Measure the ***M*** of a Gas

2) Divide the Isotope

Exercises

1. A 15.0 liter vessel containing 5.65 grams of N_2 is connected by means of a valve to a 6.0liter vessel containing 5.00 grams of oxygen. After the valve is opened and the gases are allowed to mix, what will be the partial pressure of each gas and the total pressure at 27℃?

2. Into a 5.00 liter container at 18℃ are placed 0.20mol of H_2, 20.0 grams of CO_2, and 14.0 grams of O_2. Calculate the total pressure in the container and the partial pressure of each gases.

3. P_{45}: 10